Cite this: *CrystEngComm*, 2011, **13**, 7311

www.rsc.org/crystengcomm

PAPER

An unprecedented (4,24)-connected metal–organic framework sustained by nanosized Ag_{12} cuboctahedral node†

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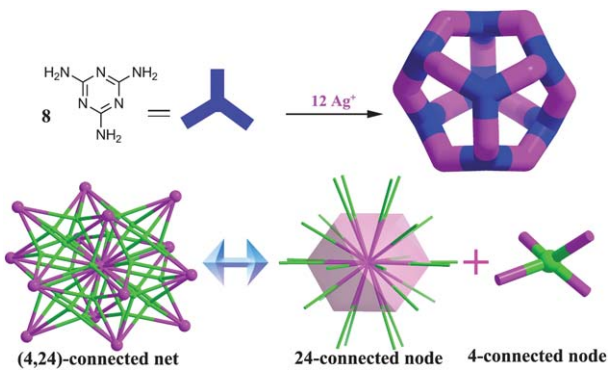
Received 3rd June 2011, Accepted 8th September 2011
DOI: 10.1039/c1ce05672g

A novel 3D metal–organic framework (MOF), namely $[Ag_{12}(MA)_8(mal)_6\cdot 18H_2O]_n$ (**1**), (MA = melamine, H_2mal = malonic acid) has been successfully synthesized through one-pot ultrasonic reaction of $AgNO_3$, MA and H_2mal and characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction. In **1**, eight tridentate MA ligands coordinate to 12 Ag(I) ions to form a nanosized Ag_{12} cuboctahedron with an interior diameter of 1.2 nm, which combines with the quadridentate mal anion to give **1**. This is a complicated 3D MOF, which is an unprecedented (4,24)-connected net with rare **twf** topology when using the Ag_{12} cage and mal as 24- and 4-connected nodes, respectively. Of particular importance, the unusual network topology and integrity of the framework of **1** after dehydration have also been validated and discussed in detail.

Introduction

Metal–organic frameworks (MOFs) based on polyhedral coordination cages are of intense interest due to not only their aesthetic appeal but also confined cavities that (i) can act as molecular flask encapsulate guest species for chemical reactivity,[1] (ii) can be used for gas separation and storage,[2] and (iii) may exhibit unusual magnetic and catalytic properties.[3] In the last couple of decades the development of self-assembly methods in transition metal coordination chemistry has led to a remarkable variety of beautiful polyhedral coordination cages with diverse sizes and shapes including tetrahedron,[4] octahedron,[5] cube,[6] dodecahedron,[7] truncated tetrahedron,[8] cuboctahedron,[9] and so on.[10] As far as we know, most of the above examples are discrete molecules containing only a single type of ligand and bivalent transition metal ions, such as Pt(II), Pd(II), Zn(II), Cd(II), Cu(II) and Co(II). However, the Ag(I) cage or its highly connected MOF with novel topology is only sporadically observed in the literature,[11] which may be because (i) the coordination preference of Ag(I) is hard to control, and (ii) Ag(I) with its d^{10} closed-shell electronic configuration has a tendency to form Ag···Ag interactions, as a result, the Ag(I) cluster becomes a frequenter in the assembly process.[12] On the other hand, the rigid MA ligand has three N donor sites located in one plane at 120° relative to each other and is expected to be a good candidate in the construction of high symmetry coordination cages, but no impressive MA transition metal complexes have appeared until now.[13] Given the above challenges and considering our previous work on the assembly of Ag(I) complexes using mixed ligand strategy,[14] herein, we report, for the first time, a binodal (4,24)-connected 3D MOF $[Ag_{12}(MA)_8(mal)_6\cdot 18H_2O]_n$ (**1**), (MA = melamine, H_2mal = malonic acid) based on a nanosized $Ag_{12}(MA)_8$ cuboctahedral cage (Scheme 1), exhibiting a rare **twf** topology, consequently filling a lacuna for 24-connected coordination nets.



Scheme 1 (Top) The scheme for the assembly of the nanosized Ag_{12} cage. (Down) The (4,24)-connected **twf** net and the two vertices and corresponding vertex figures when augmented.

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† Electronic supplementary information (ESI) available: IR and additional figure. X-Ray crystallographic data. CCDC reference numbers 843435 and 843436. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce05672g

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Experimental

Materials and methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were measured on a Nicolet 330 FTIR Spectrometer at the range of 4000–400 cm^{-1}. Elemental analyses were carried out on a CE instruments EA 1110 elemental analyzer. X-Ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-Kα radiation. TG curves were measured from 25 to 800 °C on a SDT Q600 instrument at a heating rate 5 °C min^{-1} under the N_2 atmosphere (100 mL min^{-1}).

Synthesis of $[Ag_{12}(MA)_8(mal)_6 \cdot 18H_2O]_n$ (1)

Reaction of $AgNO_3$ (85 mg, 0.5 mmol), MA (63 mg, 0.5 mmol) and H_2mal (52 mg, 0.5 mmol) in methanol/H_2O media (10 mL, v/v = 1 : 1) in the presence of ammonia (0.5 mL, 14 M) under ultrasonic treatment (160 W, 40 KHz, 50 °C). The resultant colorless solution was allowed slowly to evaporate at room temperature for one week to give colorless crystals of **1**. The crystals were isolated by filtration and washed by deionized water and dried in air. Yield: *ca.* 77% based on $AgNO_3$. Elemental analysis: Anal. calc. for **1** ($Ag_2C_7H_{16}N_8O_7$): C 15.57, H 2.99, N 20.75%. Found: C 15.97, H 2.59, N 21.53%. Selected IR peaks (cm^{-1}): 3467 (s), 3436 (s), 3167 (s), 1666 (s), 1574 (s), 1475 (m), 1448 (m), 1387 (m), 1259 (w), 1165 (w), 1013 (w), 800 (w).

X-Ray crystallography

Single-crystal X-ray diffraction data for **1** and its dehydrated phase **1′** were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer with graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å), which was equipped with an Oxford Cryosystems nitrogen gas-flow apparatus operating at 50 kV and 90 mA in ω scan mode for **1** and **1′**. A total of 44 × 5.00° oscillation images was collected, each being exposed for 10 min. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.[15] In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97[16] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[17] Atoms were located from iterative examination of difference *F*-maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C or N atoms. All structures were examined using the Addsym subroutine of PLATON[18] to assure that no additional symmetry could be applied to the models.

There are large solvent accessible void volumes in the crystals of **1**, which are occupied by disordered water molecules. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program[18] implemented in PLATON was used to remove these electron densities. The SQUEEZE function of the program PLATON reveals a residual electron density of 265 electrons/cell in cell-remaining voids where the residual electron density was tentatively assigned to one and a half water molecules per asymmetric unit of **1** [265 e/18 ≈ 15 e for per asymmetric unit of **1**; 15 e = 1.5 H_2O × 10 e/per H_2O]. The number of H_2O was also proved by the TGA and EA. The tentative formula for **1** is $[Ag_{12}(MA)_8(mal)_6 \cdot 18H_2O]_n$. A refinement using reflections modified by the SQUEEZE procedure behaved well, and the R_1 was significantly reduced from 0.0469 to 0.0205. Pertinent crystallographic data collection and refinement parameters of **1** and **1′** are collated in Table 1. Selected bond lengths, angles and hydrogen bond geometries for **1** are collated in Table 2.

Table 1 Crystal data for **1** and **1′**[a]

Complex	**1**	**1′**
Formula	$Ag_2C_7H_{16}N_8O_7$	$Ag_2C_7H_{10}N_8O_4$
M_r	540.00	485.97
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}m$	$R\bar{3}m$
a/Å	22.274(3)	22.1713(16)
c/Å	16.940(3)	16.947(2)
V/Å^3	7279(2)	7214.6(13)
T/K	173(2)	173(2)
Z	18	18
F(000)	4212	4212
μ/mm^{-1}	2.446	2.468
Ref. collected/unique	11659/1551	12124/1547
R_{int}	0.0216	0.0317
Parameters	108	108
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0205$ w$R_2 = 0.0590$	$R_1 = 0.0294$ w$R_2 = 0.0788$
R indices (all data)	$R_1 = 0.0212$ w$R_2 = 0.0594$	$R_1 = 0.0304$ w$R_2 = 0.0796$
Goodness-of-fit on F^2	1.138	1.084
Max./min., $\Delta\rho$/e Å^{-3}	0.628/−0.420	0.576/−0.457

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2 Selected bond lengths (Å), angles (°) and hydrogen bond geometries for **1**[a]

Ag1–N1	2.197(3)	Ag2–N2	2.297(2)
Ag1–N5	2.223(3)	Ag2–O2	2.367(2)
Ag1–O1^{ii}	2.630(3)		
N1–Ag1–N5	147.13(11)	N2^i–Ag2–O2	98.89(7)
N2–Ag2–N2^i	124.44(11)	N2^i–Ag2–O2^i	103.10(7)
N2–Ag2–O2	103.10(7)	O2–Ag2–O2^i	131.72(11)

D–H···*A*	H···*A*	*D*···*A*	*D*–H···*A*
N3-H3A···O2^i	2.06	2.946(3)	168.4
N3-H3B···O1^{ii}	2.03	2.924(3)	173.7
N4-H4A···O2	2.06	2.919(3)	157.9
N6-H6A···O1^{iii}	1.97	2.870(3)	176.1

[a] Symmetry codes: (i) *y*, *x*, −*z* + 2; (ii) *x* − *y* + 1/3, −*y* + 2/3, −*z* + 5/3; (iii) −*x* + 1/3, −*y* + 2/3, −*z* + 5/3.

Result and discussion

Structure description of $[Ag_{12}(MA)_8(mal)_6 \cdot 18H_2O]_n$ (1)

X-Ray single-crystal diffraction analysis reveals that **1** crystallizes in the trigonal crystal system with the space group $R\bar{3}m$, with an asymmetric unit that contains two Ag(I) ions, 2/3 MA and 1/2 mal ligands. Analysis of the local symmetry of the metal atoms and ligands shows that all of them locate in the special positions. In detail, Ag1 is bisected by the crystallographic

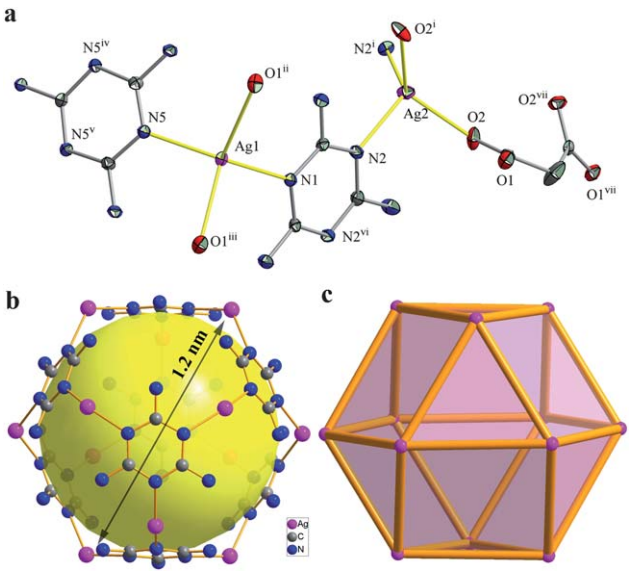

Fig. 1 (a) X-Ray crystal structure of **1**. Thermal ellipsoids are set at 50% probability. The hydrogen atoms are omitted for clarity. (b) $Ag_{12}(MA)_8$ cage. (c) Simplified cuboctahedron with alternating quadrilateral and eight triangular faces. (Symmetry codes: (i) $y, x, -z + 2$; (ii) $x - y + 1/3, -y + 2/3, -z + 5/3$; (iii) $-x + 1/3, -y + 2/3, -z + 5/3$; (iv) $-x + y, -x, z$; (v) $-y, x - y, z$; (vi) $-x + y, y, z$; (vii) $-x + 2/3, -x + y + 1/3, -z + 7/3$).

mirror plane (site occupancy factor (SOF) = 1/2); Ag2 resides on the crystallographic 2-fold axis (SOF = 1/2), which is perpendicular to the mirror plane; a MA ligand is bisected by the mirror plane (SOF = 1/2) and another one is simultaneously divided into six equal portions by two mirror planes (SOF = 1/6); a 2-fold axis passes through C2 atom of the mal (SOF = 1/2). As depicted in Fig. 1a, both Ag1 and Ag2 are located in a distorted tetrahedral geometry and coordinated by two MA and two symmetry-related mal ligands (Ag1–N1 = 2.197(3), Ag1–N5 = 2.223(3), Ag1–O1^{ii} = 2.630(4), Ag2–N2 = 2.297(2), Ag2–O2 = 2.367(2) Å). The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser[19] to describe the geometry of a four-coordinate metal system, which is 0.64 and 0.74 for Ag1 and Ag2, respectively (for perfect tetrahedral geometry, $\tau_4 = 1$). Both the Ag–N and Ag–O bond lengths are in the normal ranges as the reported complexes.[20]

The overall structure of **1** is a complicated 3D metal–organic framework containing an unprecedented Ag_{12} cage as the node and a μ_4-η^1:η^1:η^1:η^1 mal as the linker. The twelve Ag ions (6 Ag1 and 6 Ag2) are linked by eight facial triangular μ_3-MA ligands to form the $Ag_{12}(MA)_8$ cage (Fig. 1b) with the interior diameter of approximately 1.2 Å. The simplified cage has six quadrilateral and eight triangular faces with the windows of sizes (atom-to-atom distance along an edge after considering van der Waals' radii) 6.27 × 6.27 × 6.17 Å, 6.17 × 6.27 × 5.93 × 6.27 Å, 5.93 × 5.93 × 5.93 Å, respectively, which belongs to one of fifteen *Archimedean solids* - cuboctahedron (Fig. 1c).[10e] Each cuboctahedral Ag_{12} cage is linked to fourteen neighboring ones through twentyfour 4-connected tetrahedral mal ligands. This results in a (4,24)-connected 3D MOF having rare twf topology (Fig. 2a), which has only been topologically predicted by Delgado-Friedrichs and O'Keeffe as the sole edge transitive net for the assembly of truncated octahedral and tetrahedral building

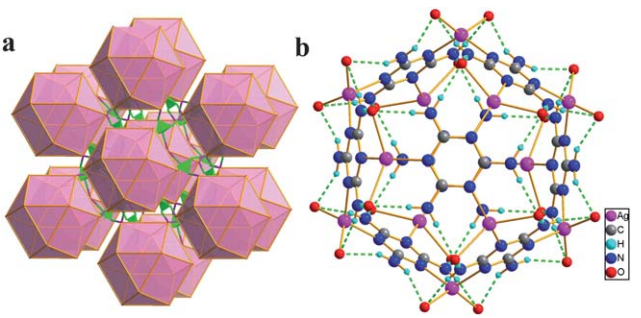

Fig. 2 (a) The (4,24)-connected **twf** network of **1**. The big cuboctahedron and the small green tetrahedron represent 24-connected and 4-connected nodes, respectively. (b) The intracage hydrogen bonds in complex **1**.

blocks.[21] No occurrence in crystal structures has been noticed to date. Notably, one strong π···π stacking interaction was found between the MA ligands of adjacent cages with the centroid···centroid distance of 3.307(2) Å (Fig. S1, ESI†). The intracage N–H···O hydrogen bonds ranging from 2.867(3) to 2.946(3) Å combined with strong π···π stacking contribute to the stability of the resulting 3D framework (Fig. 2b and Table 2). PLATON[18] calculation suggested that a solvent-accessible volume was 28.0% of the crystal volume (2034.9 Å^3 out of the 7278.6 Å^3 unit cell volume). Compared to the commonly encountered low-connected (3–8) topologies,[23] such as 3-connected **srs**, 4-connected **dia**, 6-connected **pcu**, and 8-connected **bcu** nets, (6,6)-connected **nia** and (6,8)-connected **ocu**, high-connected (>8) MOFs[24] are very scarce. This can be partially attributed to the limited coordination numbers of single metal centers and steric hindrance of the most commonly used organic ligands. As we know, the 24-connected MOF represents the highest connected topology presently known for MOFs,[25] but most of them have been restricted to (3,24)-connected MOFs,[26] so the (4,24)-connected net in complex **1** is an undocumented example. The Schläfli symbol for this net is $\{4^{120}\cdot6^{132}\cdot8^{24}\}\{4^6\}_6$ when using the Ag_{12} cage and mal as 24- and 4-connected nodes, respectively.[27]

It is also noteworthy that the present MOF can alternatively be simplified topologically as a novel three-dimensional (3,4,4)-connected trinodal net (Fig. 3) with a short Schläfli symbol of $\{6^3\}_4\{6^4\cdot8^2\}_3\{6^5\cdot8\}_6$ based on three different basic building blocks, triangular MA (3-connected node), tetrahedral Ag(I) center (4-connected node) and tetrahedral mal ligand (4-connected node). This simplified net also defines a completely new topology for three-periodic nets that is not only unobserved in

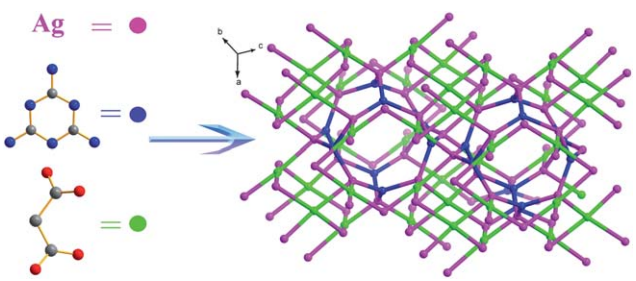

Fig. 3 The alternatively simplified (3,4,4)-connected network of **1**.

MOFs, but also unenumerated in the electronic databases EPINET, RCSR and TTD.[28]

IR spectra, X-ray powder diffraction analyses and thermal analyses

The IR spectrum (Fig. S2, ESI†) of complex **1** shows that the characteristic bands of the carboxyl groups are located at ~1660 cm^{-1} for asymmetric stretching and ~1460 cm^{-1} for symmetric stretching. The N–H asymmetric and symmetric stretching bands are ~3424 and ~3330 cm^{-1}.

In order to check the phase purity of complex **1**, the X-ray powder diffraction (XRPD) pattern of **1** was recorded at room temperature. As shown in Fig. 4, the peak positions of simulated and experimental patterns are in good agreement with each other, demonstrating the phase purity of the product. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

The thermogravimetric (TG) analysis was performed in N_2 atmosphere on polycrystalline samples of complex **1** and the TG curve is shown in Fig. 5. The TG curve of **1** exhibits three steps of weight loss. The TG curve of **1** shows the first weight loss of 9.05% in the temperature range of 25–236 °C, which indicates the loss of nine lattice water molecules per formula unit (calcd: 10.01%), and then the metal–organic framework starts to decompose until 300 °C, with the accompanying loss of MA and mal ligands. The residual weight of 40.93% is consistent with that of 39.95% calculated for metallic silver.

Based on the TG analysis, the heat-resistance of single crystals of **1** was also investigated. The freshly ground sample of **1** was placed inside a crucible of a thermogravimetric analyzer upon a heating treatment for 2 h in air at 200 °C to exclude the solvent molecules. The XRPD pattern of the solvent-free sample **1′** (Fig. 4) shows no obvious change in comparison with the simulated pattern of **1**, indicating the maintenance of periodicity of the crystalline lattice after dehydration. Single crystal X-ray diffraction on **1′** reveals that there is no changes for the backbone of the framework except that the bond lengths and angles are slightly changed (see CIF, ESI†). The careful refinement of the crystal data can give a very good *R* value (≈0.03), indicating the crystal lattice can remain intact upon extraction of lattice water molecules.

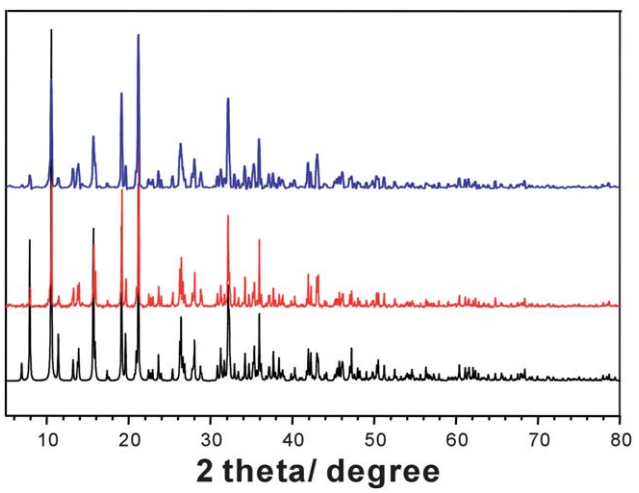

Fig. 4 Comparison of the XRPD patterns of **1** and **1′**: simulated from single crystal data of **1** (black line), the as-synthesized sample **1** (red line), and the dehydrated sample **1′** (blue line).

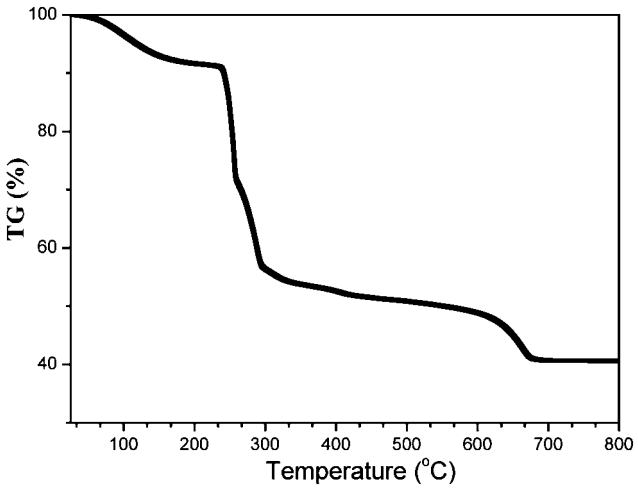

Fig. 5 The TG curve for complex **1**.

Conclusions

In conclusion, we prepared an unprecedented (4,24)-connected MOF using tripodal melamine and tetrapodal malonate anion. This net contains unusual nanosized Ag_{12} cuboctahedral cages and shows rare **twf** topology. Our innovative results highlight an important research topic and provide vision for the construction of high connected MOFs based on silver cage that have been largely underdeveloped. Moreover, the integrity of the framework of **1** after dehydration has also been validated and discussed in detail.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 20721001), 973 Project (Grant 2007CB815301) from MSTC.

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